Title :   NEW EXPANDABLE ANODE FOR DIAPHRAGM CELLS

DESCRIPTION OF THE INVENTION

The production of chlorine and caustic soda from sodium chloride solutions, the production of aluminium from molten salts and the electrometallurgy are nowadays the main electrochemical processes of industrial relevance. In particular, chlorine-caustic soda (or chlor-alkali in general) electrolysis is carried out on the basis of three types of technologies, namely the mercury cathode, diaphragm and membrane one. The latter type of electrolysis is the most advanced and represents since a few years the only option left for the construction of new plants in view of the lower electrical energy costs and of the near-zero environmental impact, while the mercury cathode and diaphragm technologies survive in already paid-off plants wherein the higher variable costs are balanced at least in part by the lower fixed costs. In order to make the operation of these plants acceptable in a situation of increasing electrical energy prices and of growing concern for human health and environment, a continuous technological improvement has been observed in the last years, which in the case of diaphragm technology has led to the development of inert fibre-based diaphragms as a replacement of the previously used asbestos and to modifications of cathode and anode design aimed at decreasing the electrical energy consumption.

Focusing the attention on the anode design, it has been particularly observed the replacement of the so-called "box" anodes with expandable-type anodes, provided with forced expansion devices, optionally of controlled action.

The "box" anodes, born as replacements of the old graphite anodes of which they substantially maintain the external shape (see for example US 3,591,483), consist of a titanium sheet provided with openings, folded so as to form an empty box (whence the name) shaped as a rectangular base prism. During the electrolyser assembly the anodes, which are secured in a multiplicity of parallel rows to a supporting and electrical current-distributing base, are intercalated between corresponding rows of cathodes, also shaped as flat boxes formed by perforated sheets or metal wire meshes coated with a porous diaphragm consisting of, as previously said, inert fibres stabilised by a polymer binder. This operation of

intercalation is quite delicate and, in order to avoid that the diaphragms be damaged by strokes or rubbing against the anodes, the same anodes have sensibly lower width than the existing gap between the rows of diaphragm-bearing cathodes. It follows that, during operation, the sensible gap existing between anodes and diaphragms (6-8 mm indicatively) entails a high voltage, to which corresponds a high electrical energy consumption.

To overcome this inconvenience, particularly heavy in times of growing electrical energy prices, expandable anodes were introduced, again shaped as a flat box, but with the two major surfaces secured to expanding devices (expanders) consisting of titanium sheets endowed with elasticity. In this way the surfaces have a certain mobility, which allows them, precisely under the push of the expanders, to get closer or farther away while remaining mutually parallel (see for example US 3,674,676). In particular, when assembling the electrolysers, the anodes are maintained in a restrained position by suitable retainers, thereby assuming a reduced width allowing to prevent damages to the diaphragms. Once positioned the anodes between rows of cathodes, the retainers are extracted leaving the anode surfaces free to expand under the effect of the intrinsic elasticity of the structure. The retainer extraction does not present any particular difficulty since in the phase of anode assemblage between the rows of cathodes, the electrolyser is free of cover, and thus the access to the anodes is entirely free.

Notwithstanding that the expansion of this kind of anode might be adjusted so as to bring the major surfaces consisting of sheets provided with apertures and catalytic coating in direct contact with the diaphragm surfaces, in the industrial practice it is preferred to maintain a gap of about 3 mm, substantially to prevent the damages which could be produced by the contact between the inevitable asperities of the sheets, whose openings are cheaply obtained by mechanical expansion, and the diaphragm whose hardness is rather modest. Indicatively, the expanded sheets are obtained making use of 1 mm thick titanium sheets as the starting material, and the expansion is adjusted so as to produce openings of typical rhomboidal shape whose diagonals are about 10 and 15 mm long. The thickness of 1 mm for the starting sheet is needed to ensure a sufficient electrical conduction, and hence a homogeneous current distribution: in its turn, such

thickness of 1 mm imposes, for the mechanical expansion, the above seen dimensions of the rhomboidal opening diagonals. With these dimensions, a partial penetration of the anode surfaces into the diaphragms cannot be avoided, leading to a further damaging to their integrity. The safety distance of about 3 millimetres is commonly ensured by introducing spacers in the form of plastic rods or buttons between the movable surfaces of the anodes and the diaphragms.

The anodes are further provided with brine recirculation means having the purpose of favouring the mass transport of chlorides toward the anode surface catalytic coating in order to facilitate the evolution of chlorine while hindering that of oxygen, which is a typical by-product of reaction. These recirculation means consist of suitable internal ducts created by sheets introduced within the "box"-type anodes, as disclosed in US 4,138,295, or by an adequate shaping of the expanders, as proposed in US 5,593,555 precisely for expandable-type anodes. In US 5,066,378 a particularly efficient recirculation device is presented, comprising baffles installed on top of the expandable anodes and connected to downcoming pipes positioned inside the anodes themselves: the baffles, which produce a rapid coalescence of the chlorine bubbles generated upon the catalytic coatings, allow to achieve a quick degassing without generating foams and therefore enhance the intensity of brine recirculation.

The finite distance between the surfaces of the diaphragms and those of the anodes after expansion entails a higher cell voltage due to the ohmic drop inside the brine film just located between such surfaces: assuming that the gas content in such film doesn't affect the electrical resistivity of brine to a substantial extent, it can be determined that to a gap of 3 mm (imposed as said above by the spacers of common use in the industrial practice) corresponds a ohmic drop of about 0.1 Volts. The real ohmic drop results considerably higher and close to 0.3 Volts when the diaphragm is of the type based on asbestos fibres mechanically stabilised with perfluorinated-type polymeric binders, still largely in use. This seriously negative situation is originated by the remarkable swelling undergone by these types of diaphragm when they are put in contact with an aqueous solution, in particular with the process brine at temperatures around 80-100°C: the diaphragm practically comes to occupy a consistent portion of the anode-diaphragm gap and therefore

the volume of brine through which the ionic migration takes place results substantially decreased, with a consequent increase of the ohmic drop for a given applied current. Although still present, the phenomenon is lower in the case of the more modern diaphragms in which, as said above, the asbestos fibres are replaced with inert fibres, for instance made of perfluorinated polymeric material and inorganic oxide such as zirconium oxide.

To eliminate or in any case reduce the above indicated ohmic drop, devices suited to compress the diaphragm so as to force it to maintain its initial thickness practically unaltered were perfected. In particular, US 5,534,122 disclosed additional elastic elements which are provided to be inserted within the expandable anodes: the purpose of the finding is to impart a force of compression to the movable anode surfaces sufficient to compensate for the push exerted by the diaphragms in the swelling phase, thereby preventing the thickness increase. The problem of damaging the delicate diaphragm under the action of the compression exerted, as seen above, by the surfaces consisting of expanded sheet, inevitably quite coarse, is solved by resorting to a composite structure comprising an expanded flattened sheet of low thickness, for example 0.3-0.5 mm, for which the mechanical working for its expansion allows to easily produce rhomboidal openings with diagonals of reduced length, for instance 3 and 5 mm, fixed to the sheet of higher thickness and wider openings of the prior art. The catalytic coating is applied to both of the expanded sheets or at least to the thin sheet. With the composite structure, a specific role is assigned to the two component sheets. In particular, the thin sheet provided with small sized openings has the purpose of blocking the diaphragm swelling by applying a much more distributed compression force: this feature, together with the regularity of the surface, substantially free of asperities as a consequence of the flattening treatment, guarantees that no significant damage is produced to the diaphragms. To the unflattened thicker sheet is deputed the task of optimally distributing the electric current while preventing the deformations which would be unavoidable with the thin sheet alone. Diaphragm chlor-alkali electrolysis cells operating at a current density of 2000 A/m² and equipped with anodes provided with the composite structure just described and with the means for brine recirculation, for

instance according to US 5,534,122, are characterised by a voltage 0.1-0.15 Volts lower than the voltages of cells provided with anodes and spacers according to the prior art. Such certainly interesting result is nevertheless inferior to the previously indicated expected value of about 0.3 Volts.

In US 4,013,525 it is described an anode consisting of vertical plates having a width of 7 mm, mutually spaced apart by 4 mm: the voltage of a diaphragm chlor-alkali cell equipped with this type of anode and working at 2000 A/m^2 results to be about 0.3 Volts better than the voltages of cells based on the current technology. A gap of 1.5-3 mm is maintained from the diaphragm, apparently to prevent the mechanical damaging produced by the contact with the edges of the plates. Such gap and the rather relevant distance between the plates do not hinder the swelling of the diaphragm in operation: therefore, at least in principle, it is legitimate to assume that the voltages of US 4,013,525 might be further improved.

An example of optimisation of the structure of a vertical anode with surfaces consisting of a multiplicity of parallel plates is given by US 4,642,173 and EP 0 203 224.

US 4,642,173, disclosing an anode for specific use in electrometallurgy cells normally free of separator, takes particularly into consideration the positive effect generated by the electrolysis surface amplification given by the surface of the catalyst-coated plates for a given external bulk: in particular, it is claimed that such amplification per unit external bulk area be comprised between 4 and 20, and preferably between 6 and 14.

In EP 0 203 224 it is described an equivalent electrode structure consisting of vertical parallel plates whereof an optimisation is proposed relating both to the amplification of the catalyst-coated surface and to the withdrawal of the gas evolved in operation: to achieve the latter objective, it is indicated that the ratio between the width of the plates and the distance thereof must be respectively maintained between 0.8 and 0.6 and between 0.2 and 0.7. In particular, the use of plates of 1-2 mm thickness and 3-5 mm width is provided. The electrode may be employed in many electrochemical applications and in particular as anode (and optionally as cathode) in diaphragm cells, with the plate edges positioned, as already seen, at a certain distance from the diaphragm to prevent mechanical

damages.

A similar structure suitable for working as anode in membrane chlor-alkali cells (which can however be employed also in diaphragm cells) is presented in US 5,290,410: in this case the structure comprises a multiplicity of vertical bars provided with catalytic coating and welded on a conductive support provided with openings for the free passage of brine: in the preferred embodiment the bars are rods of diameter comprised between 0.1 and 3 mm, spaced apart by distances of 0.5-2 times the diameter. In the text it is specifically indicated that the anode may be placed in direct contact with the ion-exchange membrane.

In US 4,469,577 it is proposed a structure consisting of plates of suitable profile disposed horizontally and slanted from the vertical plane defined by the structure itself, provided with catalytic coating. This particular kind of electrode was conceived to allow an adequate expansion of the ion-exchange membranes with which it might come in contact in membrane chlor-alkali cells. It is apparent that this electrode, likewise the types just described, cannot be placed in direct contact with diaphragms which it would penetrate under the push of the expansion devices producing mechanical damages with its edges.

From the above reported analysis of the prior art it is clear that the types of known electrode structures, developed with the purpose of amplifying the surfaces provided with catalytic coating and of promoting the withdrawal of the product gases and the recirculation of the electrolytic solutions, are not suitable for being installed as anodes in diaphragm chlor-alkali cells when the scope is minimising the production energy consumption (kWh/ton of chlorine).

This purpose is at the basis of the instant invention, which under a first aspect is directed to an electrode for cells provided with separator and particularly, although not exclusively, for diaphragm chlor-alkali cells and more particularly to an anodic structure provided with at least one movable surface suited to be installed in diaphragm chlor-alkali cells in direct contact with the diaphragm itself without any risk of mechanical damages.

In a second aspect of the invention, the movable surface is provided with elements capable of inducing an effective local recirculation of brine.

In a third aspect the invention discloses an anode for cells provided with separator,

particularly for diaphragm chlor-alkali cells, capable of ensuring a substantial reduction of the electrolysis voltage.

In a fourth aspect the anode of the invention is characterised by producing chlorine with lower oxygen contents.

In a final aspect the anode of the instant invention is characterised by reduced electric energy consumption per tonne of product chlorine.

These and other peculiar aspects of the invention are discussed in the following presentation.

DESCRIPTION OF THE FIGURES

The present invention is described making reference to the figures listed below:

- figure 1a: three-dimensional view of anode in accordance with the invention with each of the two major movable surfaces consisting of a component of higher thickness and substantially planar development resulting from a multiplicity of horizontal plates slanted with respect the vertical plane and by a further thin porous layer, for instance in form of perforated sheet, expanded sheet, mesh of wires, layer of sintered material, applied on the outer edge of the multiplicity of plates.

- figure 1b: side-view of section along line X-X of figure 1a.

- figure 1c: top-view of section along line Y-Y of figure 1a.

- figure 1d: three-dimensional view of the current collecting stem alone, provided with expanders.

- figure 2a: front-view of a particular embodiment of the plate structure of figure 1a.

- figure 2b: side-view of section along line W-W of figure 2a

- figure 3a: three-dimensional view of anode in accordance with the invention with each of the two major movable surfaces consisting of a component of higher thickness and substantially planar development resulting from a multiplicity of vertical plates and by a further thin porous layer, for instance in form of perforated sheet, expanded sheet, mesh of wires, layer of sintered material, applied on the outer edge of the multiplicity of plates.

- figure 3b: side-view of section along line K-K of figure 3a.

- figure 3c: top-view of section along line Z-Z of figure 3a.

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-       figure 4a: three-dimensional view of a further embodiment of the anode of the invention with each of the two major movable surfaces consisting of a thicker porous sheet, for instance a perforated sheet, expanded sheet, mesh of wires, layer of sintered material, with a second thin porous sheet applied thereto, also in form of perforated sheet, expanded sheet, mesh of wires, layer of sintered material.

-       figure 4b: side-view of section along line S-S of figure 4a.

-       figure 4c: top-view of section along line T-T of figure 4a.

DETAILED DESCRIPTION OF THE INVENTION

Although the finding is represented as an electrode structure suitable for being advantageously installed as anode and/or cathode on several kinds of cells provided with separator, for the sake of higher simplicity of description but without wishing to limit thereby the scopes of the present invention, reference will be made in the following to the use of this structure as anode in diaphragm chlor-alkali cells, which constitute a field of application of remarkable industrial interest.

The inventors, in their quest for an anode structure suited to functioning in diaphragm chlor-alkali cells at low voltage, reduced oxygen content in chlorine and lower energy consumption per tonne of product, and without diaphragm damaging hazard, have tested the novel types of anodic structure described in the following.

The first type of structure is represented in a three-dimensional view in figure 1a, wherein (1) indicates the current collecting stem consisting of a core of highly conductive metal such as copper provided with an external layer of corrosion resistant metal such as titanium, niobium, tantalum, (2) the foot of the stem provided with a threaded portion to allow the fixing on the supporting anodic sheet (not represented), (3) the expanders consisting of elastic elements which allow to maintain the two major surfaces in a restrained position, that is adherent to the current collecting stem, during the cell assemblage and to bring them to an expanded position, that is apart from the current collecting stem and in direct contact with the diaphragm surface (not shown) during operation as known to the experts of the field, (4) the multiplicity of parallel horizontal plates which are secured to supporting bars (6) secured in their turn to the edges of the expanders forming one of the two major surfaces, the other surface being schematised by the

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contour (10), (5) the thin porous layer consisting of an expanded flattened sheet fixed, for instance by welding, to the edges of the plates (4). In the details of figures 1b and 1c are sketched the two sections of the anode of figure 1a along the lines X-X and Y-Y respectively as side-view and as top-view. For a better understanding, in figure 1d the current collecting stem (1) provided with terminal part (2) and expanders (3) without their major surfaces is represented in three dimensions. For a better functioning, the anode of figure 1a is preferably provided with the additional expanding elements disclosed in US 5,534,122.

In figures 2a and 2b it is shown a particular embodiment of the multiplicity of plates of figure 1a, respectively as a front-view and as a side-view of the section along line W-W. In this embodiment, the horizontal plates are obtained by making cuts of suitable length in parallel and off-set horizontal rows on a sheet (7), and by subsequently deforming the sheet in correspondence of the cuts in order to form the multiplicity of plates known as "louver geometry". The advantage of this structure is given by the very quick fabrication procedure which does not require the assembling of separate plates. On the sheet provided with openings it is secured the expanded flattened thin sheet (5), as already seen for the anode of figure 1a. The assembly of sheet (7) and thin sheet (5) is in its turn fixed to the expanders (not represented) as seen in the case of the anode of figure 1a.

Figure 3d reproduces a three-dimensional view of an embodiment of anodic structure, wherein (1) indicates as already seen the current collecting stem provided with threaded foot (2) for the fixing to the anodic supporting sheet (not represented), (3) the expanders, (8) a multiplicity of vertical plates supported by the horizontal bars (9), secured to the supporting bars (6), in their turn fixed to the expanders (3); once again, the other major surface is schematised by the contour (10). The multiplicity of vertical plates (8) finally supports the expanded flattened thin sheet (5). Figures 3b and 3c respectively show a side-view and a top-view of the two sections of figure 3a along the lines K-K and Z-Z.

Finally, figure 4a reports a three-dimensional view of a further embodiment of anodic structure wherein the common parts to the previous embodiments are indicated with the same identifying numerals: the component of higher thickness consists of a sheet provided with openings (11) secured, for instance by welding,

to the above seen thin sheet (5). Figures 4b and 4c respectively show a side-view and a top-view of the two sections of figure 4a along the lines S-S and T-T.

The above disclosed anode structures were installed in lab diaphragm cells having an active area of 13 centimetre width and 100 centimetre length, equipped with the diaphragms based on asbestos fibre stabilised by polytetrafluoroethylene as binder deposited on a cathode consisting of a mesh of carbon steel wires disclosed in the examples of US 5,534,122. The cells were operated at a current density of 2500 A/m², at 90-95°C, with a purified brine feed containing 315 g/l of sodium chloride and 0.5 mg/l of calcium + magnesium and with an outlet electrolyte containing about 125 g/l of caustic soda and about 190 g/l of residual sodium chloride. The anodic structures employed had the following geometrical features:

- Type A: horizontal plates of the type shown in figure 2a, obtained by making cuts 15 millimetre long on a 1 millimetre thick sheet, in parallel and off-set horizontal rows spaced apart by 2.5 millimetres and then deforming the thus pre-cut sheet in correspondence of each of the cuts, so as to form a multiplicity of plates according to the geometry known as "louvered", with the plates slanted by 30° with respect to the vertical plan. Thin sheet obtained from 0.5 millimetre thick sheet, expanded and flattened with formation of rhomboidal openings having diagonals of 3 and 5 millimetres.

- Type B: vertical plates of the type shown in figure 3a, 4 millimetre wide, 1 millimetre thick, spaced apart by 4 millimetres. Thin sheet equivalent to that used in the anodic structure of type A.

- Type C used as reference structure, consisting, in accordance with the disclosure of US 5,534,122, of the overlap of a thin sheet equivalent to the one employed for types A and B on a sheet obtained by expansion without flattening of a 1 millimetre thick sheet with rhomboidal openings having diagonals respectively of 10 and 15 millimetres (figure 4a).

The catalytic coating employed, based on the formulation commonly used for diaphragm chlor-alkali cell anodes and consisting of a mixture of ruthenium and titanium oxides, was applied only to the thin sheet (anodes A1, B1), to both the thin sheet and the plates (anodes A2, B2), to the plates alone (anodes A3 e B3).

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As concerns type C, the coating was applied at least to the thin sheet (C1) or to both sheets, the thin and the thicker one (C2).

The results obtained can be summarised as follows:

- anode A1. Cell voltage: 2.9 Volts slowly rising in time up to 3.2 Volts after 250 hours of operation, with no further variation until the end of the test (780 hours), oxygen content in chlorine: almost constant around 3.5%.

- anode A2. Cell voltage: 2.9 Volts slowly rising up to 3.0 Volts after 200 hours of operation, with no further variation until the end of the test (850 hours), oxygen content in chlorine: fluctuating with an average value of 3.2%

- anode A3. Cell voltage: 3.0 Volts practically constant in the course of the test (990 hours), oxygen content in chlorine: about 2%

- anode B1. Cell voltage: 2.8 Volts constantly rising up to 3.1 Volts in the first 200 ore of operation, with no further variation until disassembling the cell (770 hours), oxygen content in chlorine: about 3.3%, with fluctuations of small entity.

- anode B2. Cell voltage: 2.8 Volts rising up to 3.0 volt, a value almost unvaried until the end of the test (770 hours), oxygen content in chlorine: about 3.1%

- anode B3. Cell voltage: 2.9 Volts practically unvaried in the course of the test (1050 hours), oxygen content in chlorine: 1.8%

- anodes C1 e C2. Cell voltage: 2.9 Volts with increase up to 3.3 Volts after 150 hours with no further sensible variation until the end of the test (750 hours), oxygen content in chlorine: 3.7%, fairly constant in time.

The situation resulting from the test is in principle quite surprising, since as regards the voltages, the better results should be obtained with the anodes of type A2 and B2, clearly provided with a higher overall surface with catalytic coating. In fact, this occurs with the initial voltages, which nevertheless increase in time up to values essentially similar to those of the cells equipped with anodes of type A3 and B3. A similar behaviour may perhaps be explained assuming that, under the effect of the pressure exerted by the expanding devices, an albeit moderate penetration of the thin sheet into the diaphragm surface takes place: in this way, part of its surface with the relevant catalytic coating would be blinded. Moreover, the contact between coating and diaphragm could introduce some oxygen bubbles

inside the diaphragm (chlorine should be absorbed by the alkalinity diffused from the cathode side), capable of hindering at least in part the passage of electrical current. A further negative factor is probably represented by disuniformity in the distribution of current, which tends to concentrate inside the diaphragm in correspondence of the meshes of the thin sheet when they are in contact with the diaphragm or even partially penetrating inside it. In practice after a certain period, depending on the working conditions and the nature of the diaphragm, the behaviour of anodes of types A2 and B2 would finally coincide with the one of anodes A3 and B3 wherein the catalytic coating is applied on the plates alone.

What said above also allows to understand the functioning of anodes A1 and B1 which is clearly the worst: in this case, the fact of having restricted the catalytic coating application to the thin sheet alone entails that the negative effects of blinding and of partial obstruction of the current transmission are maximised, being the compensating action of the catalytic coating, whereof the plates are free, unable to play a role.

As regards anodes A3 and B3, it would be obvious to expect a relatively high voltage value due to the higher ohmic drop in the brine, since the catalyst-coated plate surface is placed at a distance from the diaphragm corresponding to the thickness of the thin sheet. As a matter of fact, the current is redistributed along the lateral surface of the plates so that its density decreases steeply when the distance from the diaphragm increases with a parallel decrease of the ohmic drop, which thereby results substantially lower than the expected values.

The better behaviour of the anodes of family B compared to the equivalent ones of family A is likely an indication of better brine recirculation with the vertical plate structure with respect to the one with horizontal plates: the better recirculation determines in fact a quicker brine replacement also in the more blinded areas, with a favourable impact on the overall operating voltage.

Besides the values of voltage, the oxygen contents in chlorine are of great practical interest: oxygen is in fact a by-product whose formation is a useless waste of energy determining as a consequence an energy consumption increase per tonne of chlorine. Moreover, excessive levels of oxygen may cause problems in the downstream processes in which the chlorine is employed.

The higher oxygen content in chlorine characteristic of all the anodes A1, A2, B1, B2 may perhaps be explained by remembering that a certain portion of caustic soda migrates back toward the anodic compartment establishing a generally alkaline pH profile within the diaphragm, probably capable of extending also to the brine film adhering to the surface of the same diaphragm. The thin sheet provided with catalytic coating and kept in contact with the diaphragms by the expanding devices is practically in direct contact with alkaline brine: it follows a facilitated oxygen evolution up to the relatively high levels recorded during the test. The oxygen evolution is further enhanced if the thin sheet penetrates albeit partially inside the diaphragm surface.

In the case of anodes A3 and B3 the thin sheet, or equivalent structure such as for example a mesh of wires of the same thickness, is free of catalytic coating which is only applied to the plates where the alkalinity cannot arrive being dispersed by the local turbulence. The fact that the oxygen content in chlorine results lower with the B3 type anode than with the A3 one can be maybe justified by the higher local turbulence supported by the vertical plates with respect to the horizontal ones.

As said before, the oxygen content in chlorine assumes a particular importance since it directly influences the oxygen consumption per tonne of product chlorine. In particular, disregarding other factors of yield loss, such a consumption results of 2300 kWh for anode B3, better type among those utilised, to be compared with the consumption of 2450 kWh relative to anode B2, which represents the second better performance.

As regards anodes C1 and C2 (prior art) the relevant behaviour (energy consumption: 2650 kWh) is evidently of lesser value than those displayed by types A1, A2, A3, B1, B2 and B3 respectively. This result can be well interpreted in view of the working hypotheses previously exposed, particularly in view of the less effective local recirculation supported by the meshes of the thicker sheet compared to the one characteristic of the horizontal and vertical plates. A less efficient recirculation results in a lower brine replacement in the more blinded areas of the structure with consequent depletion in chlorides which is the cause of higher voltages and higher oxygen content in chlorine.

For the sake of test completion the inventors have also verified the functioning of

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an anodic structure, indicated as C3, equivalent to that of C1 and C2, with the difference in the application of the catalytic coating limited to the thicker sheet alone. A cell voltage of 3.1 Volts was recorded with no sensible variation in the course of the test (800 hours) with a slowly rising oxygen content in chlorine from an initial 2.4 % to a final 2.5 %. Thus this anode, even if characterised by not particularly brilliant performances but also higher than the anodes C1 and C2 of the prior art, can be considered for all purposes as an embodiment of the present invention, although less preferred.

In conclusion, the anodes in accordance with the present invention, consisting of a thin porous layer, such as for instance a sheet provided with openings and flattened, coupled to a porous component of higher thickness capable of promoting the local recirculation of brine, such as for instance a multiplicity of horizontal or vertical plates, with the catalytic coating only applied to such component, achieve in a satisfactory manner the objectives initially put forward of low cell voltage, low oxygen content in chlorine, contact with negligible risks of mechanical damaging with the diaphragms of chlor-alkali cells.

Several variations of the instant invention are possible, as certainly results clear to the experts of the field. Some of these are listed for the purpose of exemplifying:

-   The advantages characterising the anodes consisting of a thin expanded flattened sheet (or equivalent planar structure such as for instance a mesh of wires) and of a structure directed to favour the local recirculation of brine, are obtainable with just marginal variations also when the diaphragms are asbestos-free and consist of inert fibres, for instance made of fluorinated polymer such as polytetrafluoroethylene and/or of inorganic material such as zirconium oxide, stabilised by binders chemically resistant to the operating conditions of diaphragm chlor-alkali cells.

-   The thin sheet or equivalent structure may be made of metal or polymer, preferably hydrophilised to prevent the adhesion of gas bubbles.

-   The thin sheet or equivalent structure may have a thickness comprised between 0.1 and 1 millimetres, preferably between 0.3 and 0.5 millimetres.

-   The thin sheet may have a ratio between opening clearance and surface occupied by the construction material of at least 50%, preferably of at least 70%,

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even more preferably of at least 90%. High values of the ratio permit avoiding that local concentrations of current be created with an undue ohmic drop increase. Typical sizes, although not limiting, are: width of construction material portions 0.2-0.8 millimetres, for instance 0.5 millimetres, rhomboidal openings with major and minor diagonal respectively 1 to 5 and 3 to 7 millimetre long, for instance 3 and 5 millimetres.

- The thin sheet may be disposed directly on the diaphragms instead of being fixed to the anodic structure. In this case the pressure exerted by the anodic structure under the push of the expanding devices determines the intimate contact between the structure itself and the thin sheet, required for the functioning of the anode of the invention.

- The structures directed to promote the local recirculation of brine preferably consist of horizontal or vertical plates whose thickness, spacing and width must be optimised according to the operating conditions, in particular the current density employed, and to the diaphragm type. In principle, also considering the convenience of obtaining the highest possible coated surface and the best electrical current repartition, structures consisting of low thickness and low spacing plates result favourable. To facilitate the construction it is presumable that the minimum thicknesses should be around 0.3 millimetres, and the minimum spacing around 1 millimetre, while the width is limited by the admissible width of the anode, which although in a restrained position must be easily insertable between the cell cathode fingers. In the examples, structures comprising 15 millimetre horizontal plates obtained by deformation of a 1 millimetre thick sheet have been disclosed, but different widths, for instance comprised between 5 and 30 millimetres for plates obtained from sheets of thickness comprised between 0.3 and 2 millimetres can be likewise employed. It has been also disclosed an optimum spacing of 2.5 millimetres, but values comprised between 1 and 5 millimetres also allow to practise the invention advantageously. As regards the structure with vertical plates, 1 millimetre thick plates, with width and spacing of 4 millimetres were disclosed, but thicknesses from 0.3 to 2 millimetres for plates of width and spacing comprised between 2 and 10 millimetres could also be employed.

- With the industrial size anodes of about 0.7-1 m² per side it is probably

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difficult to exert a uniform pressure on the diaphragms whose surfaces may present planarity defects. To obviate this problem the anode is advantageously subdivided into separate sections, each secured to the expanders: the elasticity of the expanders allows a little tilt which facilitates a more uniform contact, and therefore an improved repartition of the compression, even with diaphragm characterised by sensible irregularities of planarity.

The present invention is not only relative to only newly constructed anodes, since the structure preferably consisting of the vertical or horizontal plate panels can be easily installed also on previously used anodes: the relevant procedure provides the detachment of the old expanded sheet whose catalytic coating is exhausted, the cleaning of the terminal parts of the expanders from residues of previous welds, the construction of the panels consisting of plates secured to supporting bars and provided with catalytic coating, the welding of the panels to the terminal parts of the expanders, with a final step represented for instance by the welding in case the thin sheet is made out of metal.

An entirely equivalent procedure is followed when the newly constructed anodes have lost their catalytic activity after a prolonged operation. As an alternative, it is conceivable to restore the catalytic activity by detaching the thin sheet alone and fixing in its place an expanded sheet of high thickness provided with catalytic coating and thereupon, in a position facing the diaphragms, a thin sheet or equivalent mesh free of catalytic coating. This composite structure corresponds to the type of electrode previously identified as C3: in this case, however, performances should turn out to be improved by the presence of the plate structure behind which, even with an exhausted catalytic coating, still promotes an effective local recirculation, decisive as seen above to keep the cell voltage and the oxygen content in chlorine at low levels.

The present description shall not be understood as limiting the invention, which may be practised according to further different embodiments without departing from the scopes thereof, and whose extent is solely defined by the appended claims.

In the description and claims of the present application, the word "comprise" and its variation such as "comprising" and "comprises" are not intended to exclude the

presence of other elements or additional components.